

Absorption of acoustic phonons in Fluorinated Carbon Nanotubes with non-parabolic, double periodic band.

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Abstract

We studied theoretically the absorption of acoustic phonons in the hypersound regime in Fluorine modified Carbon Nanotube (F-CNT) Γ_q^{F-CNT} and compared it to that of undoped Single Walled Nanotube (SWNT) Γ_q^{SWNT} . Per the numerical analysis, the F-CNT showed less absorption to that of SWNT thus $|\Gamma_q^{F-CNT}| < |\Gamma_q^{SWNT}|$. This is due to the fact that Fluorine is highly electronegative and weakens the walls of the SWNT. Thus, the π -electrons associated with to the Fluorine which causes less free charge carriers to interact with the phonons and hence changing the metallic properties of the SWNT to semiconductor by the doping process. From the graphs obtained, the ratio of hypersound absorption in SWNT to F-CNT at $T = 45K$ is $\frac{\Gamma_{(SWNT)}}{\Gamma_{(F-CNT)}} \approx 29$ whilst at $T = 55K$, is $\frac{\Gamma_{(SWNT)}}{\Gamma_{(F-CNT)}} \approx 9$ and at $T = 65K$, is $\frac{\Gamma_{(SWNT)}}{\Gamma_{(F-CNT)}} \approx 2$. Clearly, the ratio decreases as the temperature increases.

Keywords: Carbon Nanotube, Fluorinated, Acoustic Effects, Hypersound

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1. Introduction

Recently, acoustic effects in bulk and low dimensional materials have attracted lots of attention. This is due to the need to find coherent acoustic phonons for scientific applications as against the use of direct current [1]. Materials such as homogenous semiconductors, Superlattices (SL), Graphene and Carbon Nanotubes (CNT) are good candidates for such studies due to their properties such as the high scattering mechanism, the high-bias mean-free path (l) and their sizes which enable strong electron-phonon interaction to occur in them resulting in acoustic phonon scattering. Acoustic waves through these materials are characterized by a set of elementary resonance excitations and dynamic non-linearity which normally lead to an absorption (or amplification), Acoustoelectric Effect (AE) [2] and Acoustomagneto-electric Effect (AME) [3, 4]. The concept of acoustic wave amplification in bulk materials was predicted by Tolpygo and Uriskii(1956) [5], and in N-Ge by Pomerantz [6]. In SL, Mensah et. al. [7] studied hypersound absorption(amplification) and established its use as a phonon filter and in [8] predicted the use of the SL as hypersound generator which was confirmed in [1]. In Graphene, Nunes et. al [9] treated theoretically hypersound amplification but Dompereh et.al. [10] further proved that absorption also occurs in the material. Experimentally, Misiuk et. al. [11], Bhandu and Nash [12] studied acoustoelectric effect in Graphene.

Carbon Nanotubes (CNT) on the other hand, are cylindrical hollow rod of graphene sheets whose electronic structures are determined by the localized π -electrons in the sp^2 - hybridized bonds. Absorption (Amplification)

of hypersound in undoped CNT has been carried out theoretically by Dompreh et. al. [13, 14] and experimentally by [15, 16]. Other forms of research such as hot-electron effect [17], thermopower in CNT [18] have been carried out. Flourine-modified CNT (F-CNT) is off-late attracting a lot of scientific interest. This is attained by doping the CNT with Fluorine thus forming double periodic band CNT changing from metallic to semiconductor. As per the studies conducted by Jeon et. al. [19], absorption in F-CNT is less than that of SWNT but no studies have been done on the absorption of F-CNT in the hypersound regime. In this paper, the study of absorption of acoustic phonons in metallic SWNT and F-CNT are theoretically studied. Here, the acoustic wave considered has wavelength $\lambda = 2\pi/q$, smaller than the mean-free path of the CNT and then treated as a packet of coherent phonons (monochromatic phonons) having a δ -function distribution as

$$N(k) = \frac{(2\pi)^3}{\hbar\omega_q V_s} \phi \delta(k - q) \quad (1)$$

where k is the phonon wavevector, \hbar is the Planck's constant divided by 2π , and ϕ is the sound flux density, and ω_q and V_s are respectively the frequency and the group velocity of sound wave with wavevector q . It is assumed that the sound wave is propagated along the z -axis of the CNT.

This paper is organized as follows: In section 2, the absorption coefficient for F-CNT and SWNT are calculated. In section 3, the final equations are analyzed numerically and presented graphically. Section 4 presents the conclusion of the study.

2. Theory

Proceeding as in [20], the acoustic phonon absorption coefficient is given as

$$\Gamma_q = \frac{2\pi\phi}{\omega_q V_s} \cdot \frac{\Lambda^2 q^2}{2\sigma\omega_q} \int [f(\varepsilon(p_z + \hbar q)) - f(\varepsilon(p_z))] \delta(\varepsilon_{p_z+q} - \varepsilon_{p_z} - \hbar\omega_q) dp_z \quad (2)$$

where $f(p_z)$ is the unperturbed Boltzmann distribution function, p_z is the phonon momentum, $\varepsilon(p)$ is the energy dispersion, Λ is the deformation potential and σ is the density of the CNT. The distribution function is given as

$$f(p_z) = C \exp[-\beta(\varepsilon(p_z) - \mu)] \quad (3)$$

where μ is the chemical potential of the system, $\beta = (k_B T)^{-1}$, k_B is the Boltzmann constant, T is the absolute temperature and C is the normalization constant to be determined from the normalization condition $\int f(p) dp = m$ as

$$C = \frac{ma^2}{4\pi^2 I_o(2\gamma_o\beta) I_o(6\gamma_o\beta)} \exp[\beta(\alpha_\pi - \mu)] \quad (4)$$

m is the surface concentration of charge carriers and I_o is the modified Bessel function. For a chemically modified F-CNT, where the Fluorine atoms form a one-dimensional chain, the energy dispersion can be deduced by using the Huckel matrix method where translational symmetry is accounted for as [21]

$$\varepsilon = \alpha_\pi + \Xi_n \gamma_0 \cos^{2n-1}(ap_z) \quad (5)$$

Here $a = \sqrt{3}a_{c-c}/(2\hbar)$, Ξ is a constant, n is an integer and α_π is the minimum energy of the π -electrons within the first Brillouin zone. For $n = 2$, the

energy dispersion for F-CNT at the Fermi surface at the edge of the Brillouin zone is

$$\varepsilon(p_z) = \alpha_\pi + 8\gamma_o \cos^3(ap_z) \quad (6)$$

From energy conservation principle, the momentum (p_z) can be deduced from the delta function part of Eqn.(2) as

$$p_z = -\frac{\hbar q}{2} + \frac{1}{4a} \sin^{-1} \left(\frac{\omega_q}{12\gamma_o a q} \right) \quad (7)$$

By substituting p_z into the distribution function in Eqn.(2), and after some cumbersome calculations yields

$$\begin{aligned} \Gamma_q^{F-CNT} = \Gamma_o & \left[\sinh \left\{ 2\gamma_o \beta \sin \left(\frac{3}{2} a \hbar q \right) \sin A + 6\gamma_o \beta \sin \left(\frac{a}{2} \hbar q \right) \sin B \right\} \right. \\ & \times \cosh \left\{ 2\gamma_o \beta \cos \left(\frac{3}{2} a \hbar q \right) \cos A + 6\gamma_o \beta \cos \left(\frac{a}{2} \hbar q \right) \cos B \right\} \left. \right] \quad (8) \end{aligned}$$

where

$$\Gamma_o = \frac{ma^2}{48\pi^2 I_o(2\gamma_o \beta) I_o(6\gamma_o \beta)} \frac{\pi \phi \Lambda^2 q}{\omega_q^2 \sigma V_s \gamma_o \hbar} \frac{\Theta(1 - \alpha^2)}{\sqrt{1 - \alpha^2}}$$

where Θ is the Heaviside step function

$$A = \frac{3}{4} \sin^{-1} \left(\frac{\omega_q}{12\gamma_o a q} \right) \quad B = \frac{1}{4} \sin^{-1} \left(\frac{\omega_q}{12\gamma_o a q} \right) \quad \alpha = \frac{\omega_q}{12\gamma_o a q}$$

To compare the result with an undoped SWNT, we follow the same procedure as that of F-CNT. Using the tight-binding energy dispersion of the p_z orbital which is given as:

$$\varepsilon(p_z) = \pm \gamma_o \sqrt{1 + 4 \cos \left(\frac{\nu \pi}{n} \right) \cos \left(\frac{p_z \sqrt{3} a_{c-c}}{2\hbar} \right) + 4 \cos^2 \left(\frac{p_z \sqrt{3} a_{c-c}}{2\hbar} \right)} \quad (9)$$

where $\gamma_o = 2.6\text{eV}$ is the hopping integral parameter, $a_{c-c} = 0.142\text{nm}$ is the C-C bonding distance, and (+) and (−) signs are respectively the conduction and valence band. When $\nu = 0$, the conduction and valence bands cross each other near the Fermi points, $p_F = \pm 2\pi\hbar/3\sqrt{3}a_{c-c}$ giving the metallic nature to the armchair tube. Putting $\nu = 0$, and making the substitution, $p_z = p_z + 3p_o/2\hbar$ in Eqn.(9) gives

$$\varepsilon(p_z) = \pm\gamma_o \left(1 - 2 \cos \left(\frac{p_z \sqrt{3}a_{c-c}}{2\hbar} \right) \right) \quad (10)$$

where $p_o = 2p_F = 4\hbar\pi/3\sqrt{3}a_{c-c} \approx 1.7 \times 10^{10}\text{m}^{-1}$ see [22]. Eqn.(10) is equivalent to the energy dispersion in Eqn.(5) when $n = 1$, which is

$$\varepsilon(p_z) = \alpha_\pi + \Xi\gamma_o \cos(ap_z) \quad (11)$$

Using Eqn.(10), the absorption in SWNT is calculated as

$$\begin{aligned} \Gamma_q^{SWNT} = & \frac{\pi^2 \Lambda^2 q^2 \phi^2}{4\gamma_o^2 \omega_q^2 V_s \sigma a \sin(\frac{a\hbar q}{2})} \frac{na^2}{I_o(2\gamma_o\beta)} \\ & \times \sinh\{\beta\hbar\omega_q\} \cosh \left\{ 4\gamma_o\beta\sqrt{1-\alpha^2} \cos \left(\frac{a\hbar q}{2} \right) \right\} \frac{\Theta(1-\alpha^2)}{\sqrt{1-\alpha^2}} \end{aligned} \quad (12)$$

where

$$\alpha = \frac{\hbar\omega_q}{4\gamma_o \sin(\frac{a\hbar q}{2})}$$

3. Results and Discussion

The general expressions for the hypersound absorption in F-CNT (Γ_q^{F-CNT}) and in SWNT (Γ_q^{SWNT}) are presented in Eqn.(8) and Eqn.(12) respectively. In both equations, the absorptions are dependent on the frequency (ω_q), the

acoustic wavenumber (q), and temperature (T) as well as other parameters such as the inter-atomic distances, the velocity of sound (V_s) and the deformation potential (Λ). In both expressions (see Eqn.(8) and Eqn.(12)) a transparency window is observed: for F-CNT is $\omega_q \gg 12\gamma_o a q$; and for SWNT is $\omega_q \gg \gamma_o \sin(\frac{1}{2}a\hbar q)/\hbar$. These are the consequence of conservation laws. The Equations (8) and (13), are analyzed numerically with the following parameters used: $\Lambda = 9\text{eV}$, $q = 10^5\text{m}^{-1}$, $\omega_q = 10^{12}\text{s}^{-1}$, $V_s = 5 \times 10^3\text{m/s}$, $\phi = 10^4\text{Wb/m}^2$, and $T = 45\text{K}$. The results are graphically plotted (see Fig. 1, 2, and 3).

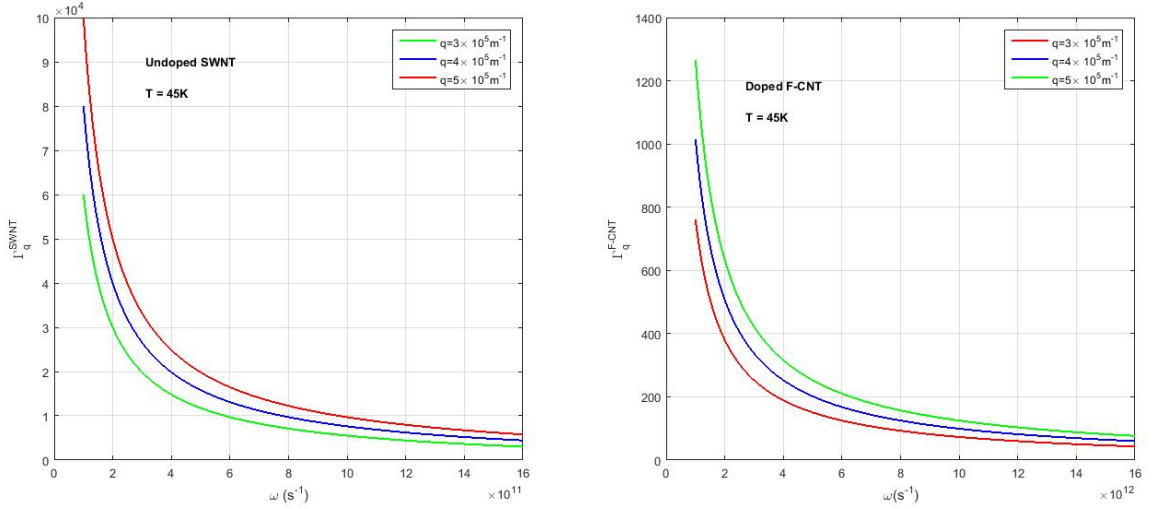


Figure 1: Dependence of Γ on ω_q (left) for an undoped SWNT, (right) for a F-CNT by varying q at $T = 45\text{K}$

Figure 1 shows the dependence of the sound absorption coefficient on the the frequency (ω_q) for varying q . In both graphs, the absorption is initially high but falls off sharply and then changes slowly at high values of ω_q . Increasing the values of q correspondingly increased the obtained graph in

both doped F-CNT and undoped SWNT though the magnitude of absorption obtained in SWNT exceeds that of F-CNT, that is, $|\Gamma_q^{SWNT}| > |\Gamma_q^{F-CNT}|$. This is in accordance with the work of Jeon et. al. [19]. In Figure 2, the

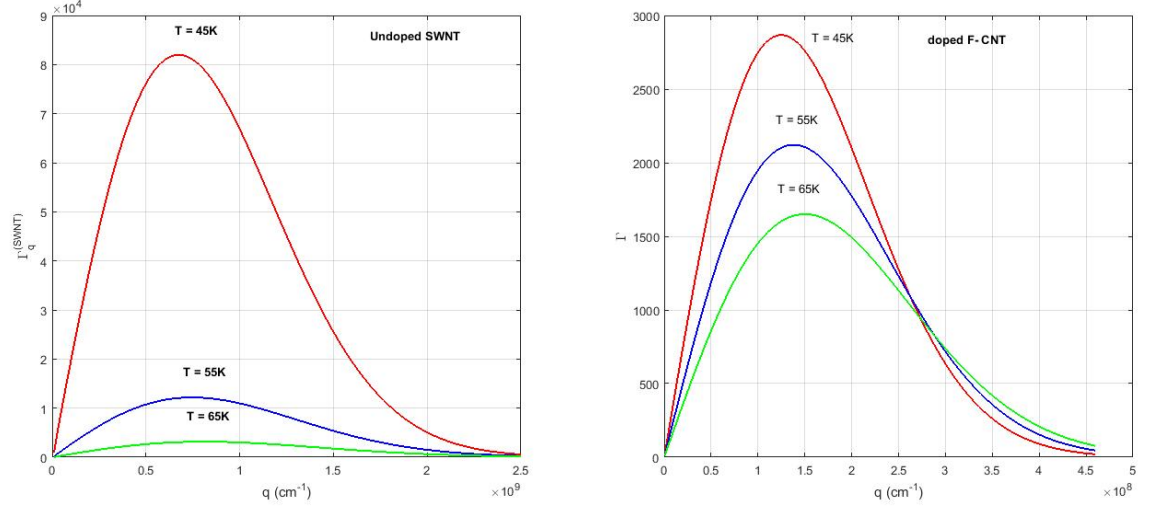


Figure 2: Dependence of Γ on q (left) for undoped SWNT and (right) for doped F-CNT at $T = 45, 55, 65K$

graph increases to a maximum point then drops off. It then changes again slowly at high q for both undoped SWNT and doped F-CNT. By increasing the temperature, the the amplitude of the graphs reduces. For $T = 45K$, the maximum absorption in $\Gamma_q^{SWNT} = 8.2 \times 10^4$ whilst that of $\Gamma_q^{F-CNT} = 2867$ which gives the ratio of the absorption $\frac{\Gamma_{(SWNT)}}{\Gamma_{(F-CNT)}} \approx 29$, whilst at $T = 55K$, $\frac{\Gamma_{(SWNT)}}{\Gamma_{(F-CNT)}} \approx 9$ and at $T = 65K$, we had $\frac{\Gamma_{(SWNT)}}{\Gamma_{(F-CNT)}} \approx 2$. Clearly, we noticed that the ratio decreases with an increase in temperature. To aid a better understanding of the comparison between the absorption obtained in both SWNT and F-CNT, a semilog plot is presented in Figure 3 which clearly shows that the undoped SWNT absorbs more than the doped F-CNT. This

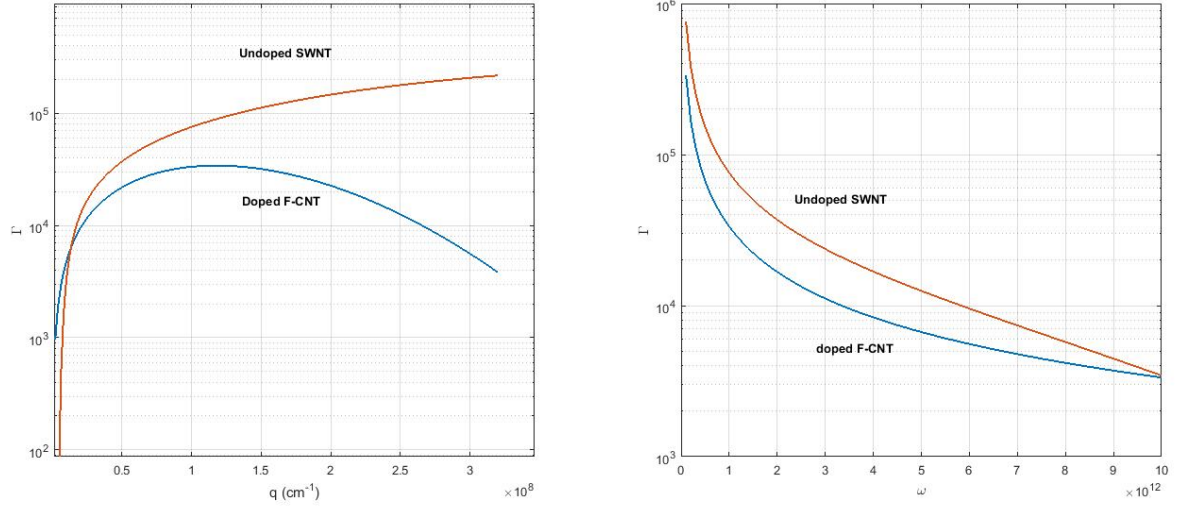


Figure 3: Semilog plot of Γ dependence on q and ω_q for doped F-CNT and undoped SWNT

can be attributed to the fact that the presence of F-CNT atoms leads to chemical activation of a passive surface CNT by adding additional electronic band structure and altering the carbon π -bonds around the Fermi level in a non-linear manner thus forming a band structure of width two periods [21]. As Flourine is highly electronegative it thus weakens the walls of the CNT as it approaches it. The π -electrons attached to the Flourine which causes less free charge carriers to interact with the phonons. Current researches have predicted sp^2 bonding charge change to sp^3 by F-functionlization [23, 24, 25]. This bonding charge change would reduce the density of free carriers, consequently leading to the magnitude reduction of the absorption [21].

4. Conclusion

The absorption of hypersound in F-CNT and SWNT was theoretically calculated in the regime $ql \gg 1$. From the numerical analysis, the graphs

of the absorptions in F-CNT and SWNT are plotted and compared. The Flourine functionalization affects the absorption properties of F-CNT. The SWNT absorbs more than the F-CNT as was observed by Jeon et. al.

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